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(54) Title: A HIGHLY HYDROPHILIC AND HIGHLY OLEOPHOBIC MEMBRANE FOR OIL-WATER SEPARATION

(57) Abstract: A polymeric membrane for separating oil from water has a pore size of 0.005  $\mu\text{m}$  to 5  $\mu\text{m}$ , a thickness of 50  $\mu\text{m}$  to 1,000  $\mu\text{m}$ , a water contact angle of 0° to 60°, an oil contact angle of 40° to 100°. The membrane contains a hydrophobic matrix polymer and a functional polymer that contains a hydrophobic backbone and side chains. The side chains each have an oleophobic terminal segment and a hydrophilic internal segment. The weight ratio of the matrix polymer to the functional polymer is 99:1 to 1:9. Also disclosed is a method of making the above described membrane.



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**A HIGHLY HYDROPHILIC AND HIGHLY  
OLEOPHOBIC MEMBRANE FOR OIL-WATER SEPARATION**

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**BACKGROUND**

Polymeric membranes are useful in separating from water dispersed or emulsified oil, which has droplet sizes below 150  $\mu\text{m}$ .

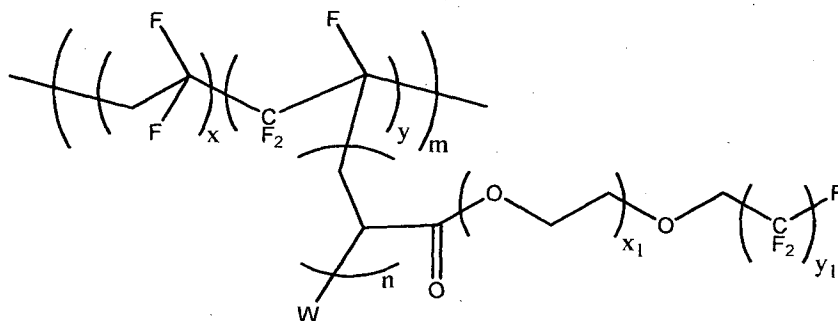
For example, ultrafiltration (UF) membranes, having a pore size of 0.01-0.1  $\mu\text{m}$ , are used to treat oily industrial wastewater. See T. Bilstad and E. Espedal, Membrane Separation of Produced Water, Water Science and Technology 34(9), 239-246 (1996). UF membranes have severe membrane fouling problems. See T. Bilstad and E. Espedal (1996); S. M. Santos and M. R. Wiesner (1997). Membrane fouling occurs when oil deposits onto a membrane surface or into its pores in a way that degrades the membrane's performance. It is a major obstacle to widespread application of UF membranes in treating oily wastewater.

Anti-fouling membranes are needed for effective and economical separation of oil from water.

**SUMMARY**

The present invention is based on an unexpected discovery of a highly hydrophilic and highly oleophobic membrane that effectively separates oil from water without significant oil fouling.

One aspect of this invention relates to a polymer of the following formula, which can be used to prepare the membrane of this invention:



25

In this formula, W is a halogen, m is 10 to 1000 (e.g., 10 to 500 or 10 to 20), n is 1 to 1000 (e.g., 5 to 500 or 5 to 10), x is 50 to 1000 (e.g., 50 to 500 or 90 to 100), y is 1 to 200 (e.g., 1 to 100 or 5 to 10),  $x_1$  is 1 to 100 (e.g., 5 to 50 or 5 to 10), and  $y_1$  is 1 to 100 (e.g., 5 to 50 or 5 to 10).

5 As shown in the above formula, this polymer includes a polyvinylidene fluoride ("PVDF") backbone and polyacrylate side chains. As also shown in this formula, each of the side chains contains an oleophobic terminal segment, i.e., a perfluoroalkyl group, and a hydrophilic internal segment, i.e., a polyethylene glycol group.

10 Another aspect of this invention relates to a membrane containing a matrix polymer that is hydrophobic and a functional polymer that is both hydrophilic and oleophobic. The functional polymer includes a hydrophobic backbone and side chains each containing an oleophobic terminal segment and a hydrophilic internal segment. Examples of the functional polymer include, but are not limited to, the polymers encompassed by the formula set forth above.

15 The just-mentioned membrane can be prepared by a method including the following steps: (i) dissolving a matrix polymer and a functional polymer in a blend solvent to obtain a blend solution, (ii) degassing the blend solution to obtain a deaerated solution, and (iii) immersing the deaerated solution into a coagulation liquid to form the polymeric membrane. If desired, one can perform the immersing step by extruding the deaerated solution into the coagulation liquid to form a hollow fiber membrane.

20 The membrane of this invention preferably has a pore size of 0.005  $\mu\text{m}$  to 5  $\mu\text{m}$  (e.g., 0.05  $\mu\text{m}$  to 0.5  $\mu\text{m}$  or 0.1  $\mu\text{m}$  to 0.3  $\mu\text{m}$ ), a thickness of 50  $\mu\text{m}$  to 1,000  $\mu\text{m}$  (e.g., 100  $\mu\text{m}$  to 500  $\mu\text{m}$  or 250  $\mu\text{m}$  to 350  $\mu\text{m}$ ), a water contact angle of 0° to 60° (e.g., 5° to 55° or 10° to 50°), and an oil contact angle of 40° to 100° (e.g., 40° to 95° or 40° to 90°). The weight ratio of the matrix polymer to the functional polymer broadly ranges from 99:1 to 1:9 (e.g., 95:5 to 6:4 or 9:1 to 7:3).

25 The details of one or more embodiments of the invention are set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description, and also from the claims.

### DETAILED DESCRIPTION

This invention provides a porous membrane for separating oil from water. The membrane is both highly hydrophilic and highly oleophobic, allowing water to pass through it while leaving oil behind.

5 The membrane, which can be a flat sheet, a hollow fiber, or a bead, has a pore size of 0.005-5  $\mu\text{m}$  and a thickness of 50-1000  $\mu\text{m}$ .

The hydrophilicity of the membrane can be quantified by water contact angle, which is preferably 0-60°. Its oleophobicity, on the other hand, can be quantified by oil contact angle, which is preferably 40-100°.

10 The membrane contains both a matrix polymer and a functional polymer.

The matrix polymer, which is hydrophobic, provides support for the membrane. Examples of the matrix polymer include, but are not limited to, PVDF, polytetrafluoroethylene, polycarbonate, polyethylene terephthalate, polypropylene, polyamide, and a combination of two or more of these polymers.

15 PVDF, as a matrix polymer, can be a homopolymer, a copolymer, a terpolymer, a higher polymer, or a combination thereof. It can contain vinylidene fluoride units greater than 70 wt.% (e.g., 75 wt.% or higher). An exemplary PVDF copolymer for use as a matrix polymer contains 71 to 99 wt.% vinylidene fluoride units and 1 to 29 wt.% hexafluoropropylene units. An operative PVDF molecular weight range is  $1.0 \times 10^4$  to  $1.0 \times 10^6$  (preferably  $1.0 \times 10^5$  to  $1.0 \times 10^6$ ,  
20 and more preferably  $4.0 \times 10^5$  to  $8.0 \times 10^5$ ). A typical commercially available PVDF has a molecular weight of  $1 \times 10^5$  to  $1 \times 10^6$ . For example, Solef® PVDF from Solvay has a molecular weight of  $4.0 \times 10^5$  to  $5.5 \times 10^5$ .

Turning to the functional polymer, it contains a hydrophobic backbone and side chains that are both hydrophilic and oleophobic. Like its side chains, the functional polymer is both  
25 hydrophilic and oleophobic.

The backbone can be PVDF, polytetrafluoroethylene, polycarbonate, polyethylene terephthalate, polypropylene, polyamide, or a combination thereof. In one embodiment, the backbone contains PVDF that has a molecular weight of  $1.0 \times 10^4$  to  $1.0 \times 10^6$  (preferably  $5.0 \times 10^4$

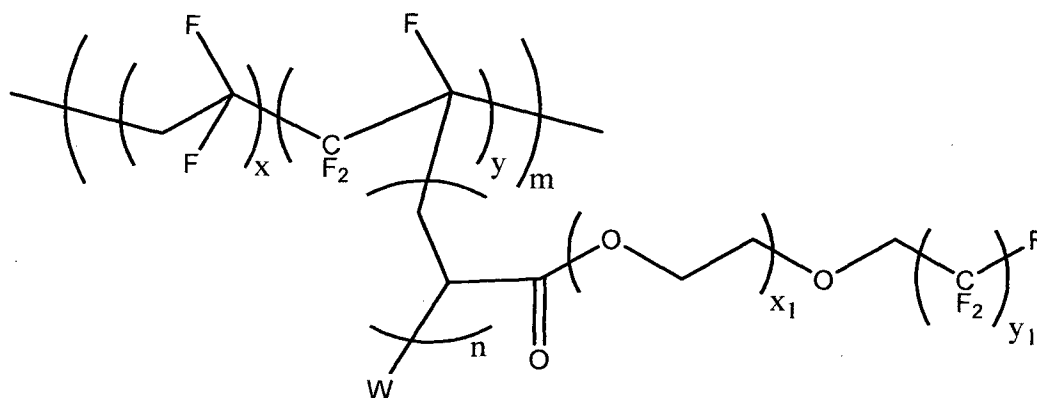
to  $5.0 \times 10^5$ , and more preferably  $1.0 \times 10^5$  to  $2.5 \times 10^5$ ). An exemplary PVDF backbone contains 71 to 99 wt.% vinylidene fluoride units and 1 to 29 wt.% chlorotrifluoroethylene units.

As for the side chains, each of them contains an oleophobic terminal segment and a hydrophilic internal segment.

5 An example of the terminal segment is a perfluoroalkyl group having a molecular weight of 40 to 4000 (preferably 200 to 2000, and more preferably 200 to 400).

Examples of the internal segment include polyethylene glycol, poly(N-vinylpyrrolidone), polyacrylamide, polyacrylic acid, polystyrenesulfonate, or a combination thereof. These internal segments have a molecular weight of 40 to 4500 (preferably 200 to 2500, and more preferably  
10 220 to 440).

The following formula encompasses functional polymers that can be used for preparing the membrane of this invention:



In this formula, W is a halogen, i.e., F, Cl, Br, and I; m can be 10 to 1000; n can be 1 to  
15 1000; x can be 50 to 1000; y can be 1 to 200; x<sub>1</sub> can be 1 to 100; and y<sub>1</sub> can be 1 to 100.

These exemplary functional polymers, both hydrophilic and oleophobic, each include a PVDF backbone and polyacrylate side chains. The side chains each contain a perfluoroalkyl terminal segment and a polyethylene glycol internal segment.

These functional polymers can be obtained as follows:

20 PVDF, e.g., poly(vinylidene fluoride-co-chlorotrifluoroethylene), is dissolved in a solvent to obtain a polymer solution. The solvent can be N-methyl-2-pyrrolidone, dimethyl formamide, dimethyl acetamide, tetramethyl urea, dimethyl sulfoxide, triethyl phosphate, or a combination thereof.

To the PVDF solution are added a ligand and a catalyst, followed by a monomer.

The ligand can be 1,1,1-tris(2-bromoisobutyryloxymethyl)ethane, 10-undecenyl 2-bromoisobutyrate, 2-hydroxyethyl 2-bromoisobutyrate, 4,4'-dinonyl-2,2'-dipyridyl, bis[2-(2'-bromoisobutyryloxy)ethyl]disulfide, dipentaerythritol hexakis(2-bromoisobutyrate), dodecyl 2-bromoisobutyrate, ethylene bis(2-bromoisobutyrate), 1,1,4,7,7-pentamethyldiethylenetriamine, octadecyl 2-bromoisobutyrate, pentaerythritol tetrakis(2-bromoisobutyrate), tris(2-pyridylmethyl)amine, tris[2-(dimethylamino)ethyl]amine, or a combination thereof.

The catalyst can be a copper catalyst, e.g., CuCl and CuBr.

The monomer can be styrene, acrylate, acrylamide, acrylonitrile, or a combination thereof, all of which contain at least a functional group that stabilizes propagating radicals. When an acrylate monomer is used, it can be methyl acrylate, ethyl acrylate, butyl acrylate, tert-butyl acrylate, 2-ethylhexyl acrylate, or a combination thereof.

The resulting mixture is heated to give a graft product, which is optionally separated or even purified from the mixture.

The graft product thus obtained is then hydrolyzed by an acid, preferably in a solvent at an elevated temperature. The acid can be HCl, H<sub>2</sub>SO<sub>4</sub>, p-toluenesulfonic acid, trifluoroacetic acid, or a combination thereof. The solvent can be toluene, N-methyl-2-pyrrolidone, dimethyl formamide, dimethyl acetamide, tetramethyl urea, dimethyl sulfoxide, triethyl phosphate, or a combination thereof.

A hydrolyzed product thus obtained is optionally separated/purified and dried.

The hydrolyzed product is then coupled with a surfactant in the presence of a coupling reagent and a catalyst to give a functional polymer in a solvent. Examples of the solvent include, but are not limited to, N-methyl-2-pyrrolidone, dimethyl formamide, dimethyl acetamide, tetramethyl urea, dimethyl sulfoxide, triethyl phosphate, and a combination thereof.

The surfactant is both hydrophilic and oleophobic. It can be a fluorosurfactant containing a hydroxyl group.

The coupling reagent can be dicyclohexylcarbodiimide, diisopropylcarbodiimide, ethyl-(N',N'-dimethylamino)propylcarbodiimidehydrochloride, or a combination thereof.

The catalyst can be 4-(dimethylamino)-pyridine, beta,beta,beta-tribromoethyl ester, tributylphosphine, scandium trifluoromethanesulfonate, trimethylsilyl trifluoromethanesulfonate, diphenylammonium trifluoromethanesulfonate, pentafluoroanilinium trifluoromethanesulfonate, or a combination thereof.

5 The functional polymer is optionally separated/purified and dried.

The functional polymer thus made can be used to prepare the membrane of this invention following the procedures described below:

10 A blend solution is obtained by dissolving a matrix polymer and a functional polymer (e.g., 10 to 30 wt.% combined) in a blend solvent, and, optionally, stirred (e.g., at 800 rpm) for an extended period of time (e.g., 2 hours). It is preferred that the blend solution be prepared in an air-tightly sealed vessel to prevent evaporation of the solvent.

15 A blend solvent is a solvent that can dissolve a matrix polymer and a functional polymer and is miscible with a coagulation liquid. Examples of the blend solvent include, but are not limited to, tetrahydrofuran, methyl ethyl ketone, dimethyl formamide, dimethyl acetamide, tetramethyl urea, dimethyl sulfoxide, trimethyl phosphate, N-methyl-2-pyrrolidone, butyrolacetone, isophorone, carbitor acetate, or a mixture thereof. If necessary, one can obtain a homogeneous polymer blend solution by heating and subsequent cooling and filtration.

20 The blend solution thus obtained is then degassed to free any air bubbles entrapped therein, e.g., through centrifuging this solution. The time needed for degassing depends on viscosity of the solution.

After degassing, the polymer blend solution is immersed, preferably at 20 to 100 °C, and more preferably at 60 to 80 °C, into a coagulation liquid to form a membrane of this invention.

25 The coagulation liquid, i.e., a coagulation nonsolvent as generally known in the field, is a liquid that is miscible with a blend solvent and its addition to a blend solution results in formation of a polymeric membrane. The coagulation liquid can be water, methanol, ethanol, propanol, isopropanol, or a mixture thereof.

If desired, the immersion of a blend solution and a coagulation liquid can be performed by extruding the blend solution into the coagulation liquid to form a hollow fiber membrane, using a wet spinning apparatus. For example, through a spinneret, a blend solution is extruded.

into a coagulation liquid with simultaneous delivery by a syringe pump of the same or a different coagulation liquid to the lumen of the fiber thus formed. The distance between the surface of the coagulation liquid and the outlet of the spinneret, i.e., the air gap, can be 0 to 50 cm, depending on the pore size and surface roughness of the hollow fiber membrane to be prepared. Generally, a greater air gap results in a membrane having a lower permeation flux and a higher solute separation performance. The flow rate of the blend solution extruding into the coagulation liquid can be controlled by compressed nitrogen gas. The coagulation liquid passing the lumen of the fiber can be controlled by a syringe pump that feeds the coagulation liquid to the spinneret.

A person skilled in the art can determine without undue experimentation conditions for preparing the membrane of this invention, such as relative concentrations of all reactants, temperature for mixing/reaction, duration of reaction/mixing/degassing, flow rates of polymer blend solutions and coagulation liquids, and sizes of filters and spinnerets.

The specific examples below are to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever. Without further elaboration, it is believed that one skilled in the art can, based on the description herein, utilize the present invention to its fullest extent. All publications cited herein are incorporated by reference in their entirety.

#### Example 1: Preparation of a functional polymer:

Poly(vinylidene fluoride-co-chlorotrifluoroethylene) was dissolved in N-methyl-2-pyrrolidone in an air-tight flask purged with N<sub>2</sub>. The mixture was stirred at 200 to 1000 rpm and heated at 60 to 90 °C to obtain a homogeneous and viscous polymer solution. The polymer concentration was 10-30 wt.%.

To the above solution were added CuCl (1-5 wt.%) and pentamethyldiethylenetriamine (2-10 wt.%), followed by tert-butyl acrylate (10 to 50 wt.%).

The resulting mixture was heated to 50 to 90 °C for 0.5 to 4 hours. Upon cooling, the mixture was poured into water to precipitate a graft product containing polyacrylate side chains, which was washed with water.

The graft product (1 to 10 g) was stirred in p-toluenesulfonic acid toluene solution (100 mL, 10-30 wt.%) at 80 to 95 °C for 4 to 8 hours. Upon cooling, the acidic solution was poured into water, washed with water, and dried in a freeze drier to yield a hydrolyzed product containing poly(acrylic acid) side chains.

5 To the hydrolyzed product solution in dimethylformamide (4-8 wt.%) were added Zonyl® FSN-100 fluorosurfactant (molecular weight 950, 2-4 wt.%), dicyclohexylcarbodiimide (0.5-1 wt.%), and 4-(dimethylamino)-pyridine (0.01-0.05 wt.%). The resulting mixture was stirred at an ambient temperature for 48-120 hours, then poured into water, washed with water and dried in a freeze drier to yield a functional polymer.

10

#### EXAMPLE 2: Preparation of a polymer blend solution

To dimethylformamide were added PVDF and the functional polymer prepared in Example 1 (10-30 wt.% combined, PVDF : functional polymer = 7:3) in a tightly sealed vessel that was heated to 70 to 100 °C. The mixture was stirred at 400 to 1000 rpm for 1-5 hours and  
15 cooled to an ambient temperature to obtain a blend solution.

The blend solution was filtered in an air-tight stainless steel dope tank and was forced, under 2 bar pressure by compressed nitrogen gas, through a 15 µm stainless steel filter.

The filtered blend solution was degassed by centrifuging the solution at 3000 to 8000 rpm for 5 to 10 minutes.

20

#### EXAMPLE 3: Fabrication of a hollow fiber membrane

A spinning apparatus containing a spinneret having an OD/ID of 1.5/0.5 mm was used to extrude the blend solution of Example 2, driving by compressed nitrogen gas, into a water bath to form a hollow fiber membrane. Simultaneously, a syringe pump fed water into the lumen of  
25 the fiber through an annular ring inside the spinneret.

The air gap was 0.5 cm. Compressed nitrogen gas was used to keep the flow rate of the polymer blend solution at 4 mL/min. The syringe pump was used to control the flow rate of water at 1 mL/min. The coagulant temperature was 60 to 80 °C.

Finally, the hollow fiber membrane thus obtained was dried in air.

#### EXAMPLE 4: Measurement of oil removal efficiency

The hollow fiber membrane prepared in Example 3 was studied as to its efficiency in removing emulsion crude oil from water.

A membrane filtration experiment was conducted on a dead-end filtration system, powered by a micro pump (ISMATEC IP65) with a pump head (Micropump, 170-000) providing motivation flow and pressure. Oil concentrations were detected with the TOC analyzer (SHIMADZU, TOC-V). Permeate weights were measured by a digital balance (M.R.C.,  $\beta\beta$ -1550) that was linked to a computer for data collection and permeate flux calculation. An oil/water emulsion (500 ppm) was prepared by mixing 0.5 g of hexadecane and 1 L water in a homogenizer (Cole-Parmer, Labgen 700) at 14,000 rpm for 20 min.

It was unexpected that the membrane separated oil from water most efficiently as shown in the results below:

Oil removal efficiency 99%

Cycle 1:

|       |  |
|-------|--|
| $J_0$ | 54.93 L·m <sup>-2</sup> ·h <sup>-1</sup> |
| RFD   | 49%                                      |
| RFR   | 71%                                      |
| RFR_B | 99%                                      |

Cycle 2:

|        |  |
|--------|--|
| $J_0$  | 54.49 L·m <sup>-2</sup> ·h <sup>-1</sup> |
| RFD_1  | 52%                                      |
| RFR_1  | 68%                                      |
| RFR_B1 | 99%                                      |

$J_0$  is permeate flux, RFD is relative flux decline of cycle 1, RFR is relative flux recovery of Cycle 1, RFR\_B is relative flux recovery after 30 min backwashing of Cycle 1, RFD\_1 is relative flux decline of cycle 2, RFR\_1 is relative flux recovery of Cycle 2, and RFR\_B1 is relative flux recovery after 30 min backwashing of Cycle 2.

Also unexpectedly, the membrane demonstrated strong resistance to oil fouling as evidenced by low relative flux decline and high relative flux recovery.

### OTHER EMBODIMENTS

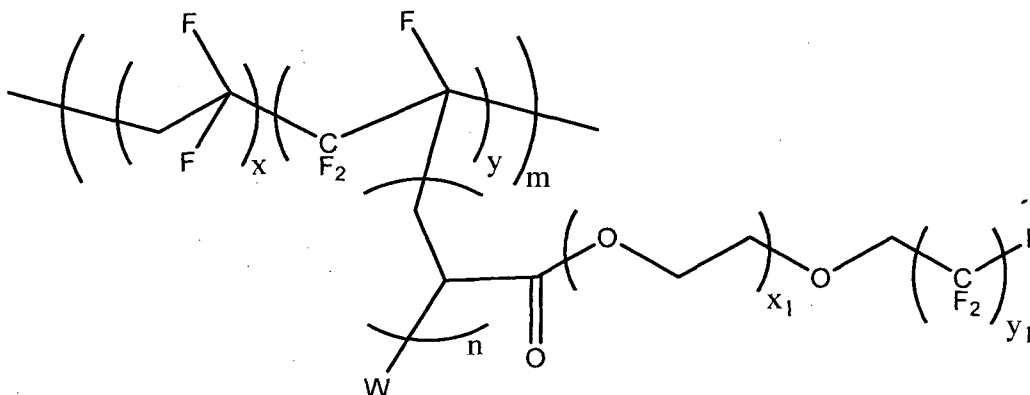
5 All of the features disclosed in this specification may be combined in any combination. Each feature disclosed in this specification may be replaced by an alternative feature serving the same, equivalent, or similar purpose. Thus, unless expressly stated otherwise, each feature disclosed is only an example of a generic series of equivalent or similar features.

10 Indeed, to achieve the purpose of separating oil from water, one skilled in the art can design a membrane that contains any combination of hydrophilic side chains, oleophobic side chains, and hydrophilic and oleophobic side chains. Further, the ratios, lengths, and densities of these side chains can be so engineered to allow water to pass through the membrane while leaving oil behind.

15 From the above description, a skilled artisan can easily ascertain the essential characteristics of the present invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Thus, other embodiments are also within the claims.

**WHAT IS CLAIMED IS:**

1. A polymer of the following formula:



wherein W is a halogen, m is 10 to 1000, n is 1 to 1000, x is 50 to 1000, y is 1 to 200,  $x_1$  is 1 to 100, and  $y_1$  is 1 to 100.

2. The polymer of claim 1, wherein m is 10 to 500, n is 5 to 500, x is 50 to 500, y is 1 to 100,  $x_1$  is 5 to 50, and  $y_1$  is 5 to 50.
3. The polymer of claim 2, wherein m is 10 to 20, n is 5 to 10, x is 90 to 100, y is 5 to 10,  $x_1$  is 5 to 10, and  $y_1$  is 5 to 10.
4. A polymeric membrane for separating oil from water, the membrane comprising:  
 a matrix polymer that is hydrophobic, and  
 a functional polymer that contains a hydrophobic backbone and side chains, the side chains each having an oleophobic terminal segment and a hydrophilic internal segment,  
 wherein the membrane has a pore size of 0.005  $\mu\text{m}$  to 5  $\mu\text{m}$ , a thickness of 50  $\mu\text{m}$  to 1,000  $\mu\text{m}$ , a water contact angle of 0° to 60°, an oil contact angle of 40° to 100°, and a weight ratio of the matrix polymer to the functional polymer of 99:1 to 1:9.

5. The membrane of claim 4, wherein the membrane has a pore size of 0.05  $\mu\text{m}$  to 0.5  $\mu\text{m}$ , a thickness of 100  $\mu\text{m}$  to 500  $\mu\text{m}$ , a water contact angle of 5° to 55°, an oil contact angle of 40° to 95°, and a weight ratio of the matrix polymer to the functional polymer of 95:5 to 6:4.
- 5
6. The membrane of claim 5, wherein the membrane has a pore size of 0.1  $\mu\text{m}$  to 0.3  $\mu\text{m}$ , a thickness of 250  $\mu\text{m}$  to 350  $\mu\text{m}$ , a water contact angle of 10° to 50°, an oil contact angle of 40° to 90°, and a weight ratio of the matrix polymer to the functional polymer of 9:1 to 7:3.
- 10
7. The membrane of claim 4, wherein the matrix polymer is polyvinylidene fluoride, polytetrafluoroethylene, polycarbonate, polyethylene terephthalate, polypropylene, polyamide, or a combination thereof; the backbone is polyvinylidene fluoride, polytetrafluoroethylene, polycarbonate, polyethylene terephthalate, polypropylene, polyamide, or a combination thereof; the oleophobic terminal segment is a perfluoroalkyl group; the hydrophilic internal segment is polyethylene glycol, poly(N-vinylpyrrolidone) group, polyacrylamide, polyacrylacid, polystyrenesulfonate, or a combination thereof.
- 15
8. The membrane of claim 7, wherein the membrane has a pore size of 0.05  $\mu\text{m}$  to 0.5  $\mu\text{m}$ , a thickness of 100  $\mu\text{m}$  to 500  $\mu\text{m}$ , a water contact angle of 5° to 55°, an oil contact angle of 40° to 95°, and a weight ratio of the matrix polymer to the functional polymer of 95:5 to 6:4.
- 20
9. The membrane of claim 8, wherein the membrane has a pore size of 0.1  $\mu\text{m}$  to 0.3  $\mu\text{m}$ , a thickness of 250  $\mu\text{m}$  to 350  $\mu\text{m}$ , a water contact angle of 10° to 50°, an oil contact angle of 40° to 90°, and a weight ratio of the matrix polymer to the functional polymer of 9:1 to 7:3.
- 25

10. The membrane of claim 7, wherein the matrix polymer is polyvinylidene fluoride, and the functional polymer is the polymer of claim 1.
11. The membrane of claim 10, wherein the membrane has a pore size of 0.05  $\mu\text{m}$  to 0.5  $\mu\text{m}$ , a thickness of 100  $\mu\text{m}$  to 500  $\mu\text{m}$ , a water contact angle of 5° to 55°, an oil contact angle of 40° to 95°, and a weight ratio of the matrix polymer to the functional polymer of 95:5 to 6:4.
12. The membrane of claim 11, wherein the membrane has a pore size of 0.1  $\mu\text{m}$  to 0.3  $\mu\text{m}$ , a thickness of 250  $\mu\text{m}$  to 350  $\mu\text{m}$ , a water contact angle of 10° to 50°, an oil contact angle of 40° to 90°, and a weight ratio of the matrix polymer to the functional polymer of 9:1 to 7:3.
13. The membrane of claim 7, wherein the matrix polymer is polyvinylidene fluoride, and the functional polymer is the polymer of claim 2.
14. The membrane of claim 13, wherein the membrane has a pore size of 0.05  $\mu\text{m}$  to 0.5  $\mu\text{m}$ , a thickness of 100  $\mu\text{m}$  to 500  $\mu\text{m}$ , a water contact angle of 5° to 55°, an oil contact angle of 40° to 95°, and a weight ratio of the matrix polymer to the functional polymer of 95:5 to 6:4.
15. The membrane of claim 14, wherein the membrane has a pore size of 0.1  $\mu\text{m}$  to 0.3  $\mu\text{m}$ , a thickness of 250  $\mu\text{m}$  to 350  $\mu\text{m}$ , a water contact angle of 10° to 50°, an oil contact angle of 40° to 90°, and a weight ratio of the matrix polymer to the functional polymer of 9:1 to 7:3.
16. The membrane of claim 7, wherein the matrix polymer is polyvinylidene fluoride, and the functional polymer is the polymer of claim 3.

17. The membrane of claim 16, wherein the membrane has a pore size of 0.05  $\mu\text{m}$  to 0.5  $\mu\text{m}$ , a thickness of 100  $\mu\text{m}$  to 500  $\mu\text{m}$ , a water contact angle of 5° to 55°, an oil contact angle of 40° to 95°, and a weight ratio of the matrix polymer to the functional polymer of 95:5 to 6:4.

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18. The membrane of claim 17, wherein the membrane has a pore size of 0.1  $\mu\text{m}$  to 0.3  $\mu\text{m}$ , a thickness of 250  $\mu\text{m}$  to 350  $\mu\text{m}$ , a water contact angle of 10° to 50°, an oil contact angle of 40° to 90°, and a weight ratio of the matrix polymer to the functional polymer of 9:1 to 7:3.

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19. A method for making a polymeric membrane comprising:

dissolving a matrix polymer and a functional polymer in a blend solvent to obtain a blend solution,

degassing the blend solution to obtain a deaerated solution, and

15 immersing the deaerated solution into a coagulation liquid to form the polymeric membrane,

wherein the matrix polymer is hydrophobic and the functional polymer contains a hydrophobic backbone and hydrophilic side chains, the side chains each having an oleophobic terminal segment and a hydrophilic internal segment.

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20. The method of claim 19, wherein the immersing step is performed by extruding the deaerated solution into the coagulation liquid to form a hollow fiber membrane.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2012/000152

|  |   |  |   |
|--|---|--|---|
| <b>A. CLASSIFICATION OF SUBJECT MATTER</b>   |   |  |   |
| B01D 71/34 (OCT 2005)<br>C08F 259/08 (OCT 2005)  | B01D 71/78 (OCT 2005)<br>C08F 214/22 (OCT 2005)   | B01D 71/82 (OCT 2005)<br>C08F 214/26 (OCT 2005)  | B01D 61/18 (OCT 2005)<br>C08F 214/28 (OCT 2005) |
| According to International Patent Classification (IPC) or to both national classification and IPC  |   |  |   |
| <b>B. FIELDS SEARCHED</b>  |   |  |   |
| Minimum documentation searched (classification system followed by classification symbols)  |   |  |   |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  |   |  |   |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br>HCAPLUS, EPODOC, WPI: Keywords: (PVDF; VINYLIDENE FLUORIDE; GRAFT; SIDE CHAIN; COMB POLYMER; HYDROPHILIC; MEMBRANE; OLEOPHOBIC and associated terms) |   |  |   |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>  |   |  |   |
| Category*  | Citation of document, with indication, where appropriate, of the relevant passages  |  | Relevant to claim No.                           |
|  | Documents are listed in the continuation of Box C   |  |   |
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| * Special categories of cited documents:   |   |  |   |
| "A" document defining the general state of the art which is not considered to be of particular relevance   | "T"   | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  |   |
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| Date of the actual completion of the international search<br>22 June 2012  | Date of mailing of the international search report<br>26 June 2012  |  |   |
| Name and mailing address of the ISA/AU<br>AUSTRALIAN PATENT OFFICE<br>PO BOX 200, WODEN ACT 2606, AUSTRALIA<br>Email address: pct@ipaaustralia.gov.au<br>Facsimile No.: +61 2 6283 7999  | Authorized officer<br>Benjamin Silva<br>AUSTRALIAN PATENT OFFICE<br>(ISO 9001 Quality Certified Service)<br>Telephone No. +61 3 9935 9611 |  |   |

## INTERNATIONAL SEARCH REPORT

International application No.

C (Continuation).

DOCUMENTS CONSIDERED TO BE RELEVANT

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| Category* | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/SG2012/000152**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| <b>Patent Document/s Cited in Search Report</b> |                         | <b>Patent Family Member/s</b> |                         |
|---|-------------------------|-------------------------------|-------------------------|
| <b>Publication Number</b>                       | <b>Publication Date</b> | <b>Publication Number</b>     | <b>Publication Date</b> |
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